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RELAXATION TIMES AND NORMAL MODE FREQUENCIES

by

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In this note we shall show that in a uniformly damped solid, there is a simple relationship between normal mode frequencies and corresponding relaxation times. The solution of the relaxation time distribution function problem thereby reduces to obtaining the normal mode frequency spectrum of the array. This connection was previously postulated by one of us[1], and is proven (within certain limitations) in this note.

The thermal energy of a crystal or glass containing N particles is reflected in the small vibrations of these particles about their equilibrium positions in the lattice. The collective motion can be analyzed in terms of normal mode lattice vibrations, each mode having a characteristic frequency. The frequency distribution is of great importance in calculating the specific heat of the solid. For the one-dimensional array, an exact frequency distribution has been derived in the classic work of Born and von Karman[2]. For an isotropic three-dimensional solid, the frequency distribution may only be approximated (Debye, Blackman, etc.[2]).

Consider a lattice in which the motion of each particle is uniformly damped. The equation of motion of the j^{th} particle in the absence of external forces is:

$$m\ddot{x}_j + f\dot{x}_j + \sum_{i=1}^{N} a_{ij}x_j = 0 \qquad (1)$$

$j = 1, 2, \ldots, N,$

where $x_j(t)$ is the displacement from equilibrium of the j^{th} bead of mass m and friction factor f. The quantities a_{ij} represent the interaction force constants between the i^{th} and j^{th} particles. In a one-dimensional lattice with nearest neighbor interactions only, the sum reduces to:

$$\alpha(2x_j - x_{j-1} - x_{j+1}) \tag{2}$$

where α is the force constant between adjacent particles.

Equation (1) may be put in the form:

$$m\ddot{q}_n + f\dot{q}_n + k_n q_n = 0 \tag{3}$$

$$n = 1, 2, \ldots, N$$

by an appropriate transformation of coordinates. The $q_n(t)$ are the normal coordinates of the motion.

Equation (3) is readily solved, and with the initial conditions that $q_n(0) =$ const. and $\dot{q}_n(0) = 0$,

$$q_n(t) = \frac{q_n(0)}{s_+^n - s_-^n}\left(s_+^n\, e^{-s_-^n t} - s_-^n\, e^{-s_+^n t}\right) \tag{4}$$

where

$$s_\pm^n = \frac{f}{2m}\left[1 \pm \sqrt{1 - \delta_n}\,\right] \tag{5}$$

with

$$\delta_n = 4mk_n/f^2$$

Now in the strongly overdamped limit ($\delta_n \to 0$) and for times longer than $t = 4m/f(4 - \delta_n)$, the first term of Equation (4) dominates and the normal mode displacement decays in time according to:

$$\langle q_n(0)q_n(t)\rangle \cong \langle q_n^2(0)\rangle\, e^{-t/\tau_n} \tag{6}$$

where $\tau_n = f/m\,\omega_n^2$

$$\omega_n = (k_n/m)^{\frac{1}{2}} \tag{7}$$

ω_n is the characteristic angular frequency of the undamped mode. Equation (7) for the relaxation time associated with the n^{th} normal mode is fundamental in the present work and is seen to be independent of the dimensionality of the oscillator array. Such a relation was proposed to hold in all dimensions by one of us in 1962[1]. We see here that the postulate is true in the overdamped case and at long times. For very short times, $q_n(t)$ decays as a Gaussian.

The Rouse-Bueche (RB) theory[3,4] of polymer viscoelasticity can be derived as a special case of the equations presented here. Since we are dealing with a linear lattice in this case, equation (2) must be substituted for the third term in equation (1). The constant α for the RB theory is an entropic force constant (from rubber elasticity theory) equal to $3kT/\sigma^2$ where σ^2 is the mean square length of a Gaussian segment. The frequencies, ω_n, are given by the Born-von Karman solution, namely

$$\omega_n^2 = \frac{4\alpha}{m}\sin^2\frac{n\pi}{2N} \qquad n = 1,2,\ldots,N \tag{8}$$

(The normal coordinate treatment of the linear lattice is given in Wannier[5].) The relaxation times are related to the frequencies by our general solution, Equation (7), and hence are

$$\tau_n = f/4\alpha\,\sin^2\frac{n\pi}{2N} \cong \frac{fN^2}{\alpha\pi^2 n^2},\ \text{for large N} \qquad n = 1,2,\ldots,N \tag{9}$$

In our general theory, presented in Equations (1-7), the force constants may be of any type (energetic or entropic) and Equation (7) is valid for a lattice in one, two or three dimensions. Equation (7) provides a unique connection between the relaxation time spectrum and the frequency distribution as discussed in reference 1. An application of Equation (7) to the theory of the viscoelastic response of polymeric - and simple organic - glasses is discussed in reference (6).

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A simple relationship between normal mode frequencies and relaxation times known to hold for damped one dimensional solids has been proven to obtain in all dimensions. Utilizing this relationship, the solution of the relaxation time distribution function problem reduces to the consideration of normal mode frequency spectrum of the array in question, irregardless of dimensionality.

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